

## **Ultrafine Modified Aluminum Hydroxide and Its Preparation**

### **Field of the invention**

The present invention relates to a preparation method of ultrafine modified aluminum hydroxide ( $\text{Al}(\text{OH})_3$ ) under high gravity field in rotating beds and modifying condition, as well as modified product of  $\text{Al}(\text{OH})_3$  via this method. And also, the invention relates to the precursor of modified  $\text{Al}(\text{OH})_3$ , that is to say, preparation method of ultrafine  $\text{Al}(\text{OH})_3$  and nanoscale  $\text{Al}(\text{OH})_3$  product thereof.

### **Background of technology**

Aluminum hydroxide has been widely used in many fields such as chemical industry, ceramics, paint and paper making, et al. Because of its superfine particle size, ultrafine  $\text{Al}(\text{OH})_3$  has many significant merits that common  $\text{Al}(\text{OH})_3$  does not have. For example, used as fire retardant, it can greatly improve fire retardation. Meanwhile, it can be used as precursor compound of ultrafine aluminum oxide, and used to prepare high activated catalyst. It can be applied to bio-ceramics and inorganic/organic nano-composite materials, and so on.

Traditional preparation method of  $\text{Al}(\text{OH})_3$  is to precipitate  $\text{Al}(\text{OH})_3$  from sodium aluminate ( $\text{NaAlO}_2$ ) solution. The common methods of precipitation include inoculating seed decomposition method where seed crystal is added to  $\text{NaAlO}_2$  solution, and carbon component decomposition method where  $\text{CO}_2$  is introduced into  $\text{NaAlO}_2$  solution. These two kinds of methods are mostly mature in industry nowadays, while  $\text{Al}(\text{OH})_3$  product is always metallurgy grade having a particle size from tens to hundreds of micrometer. In order to acquire superfine particle, somebody attempted to expand and explore traditional method and achieved some new methods, such as Emile Trebillon (see US patent US 4,492,682), Bernard F. Armbrust (see US patent US 3,268,295). They use carbon component decomposition that introduces  $\text{CO}_2$  into  $\text{NaAlO}_2$  solution with severe stirring to generate gel. After washing and filtering, the gel is dispersed in other solution to get ultrafine  $\text{Al}(\text{OH})_3$  product after heating treatment. Nevertheless, the time of carbon component decomposition is too long. When solution volume is only 0.5 litre, carbon component decomposition process needs another 15~30min to terminate the reaction. Moreover, efficiency is low, and the attained gel is not uniform.

See that all engineering plastics and peculiar plastics are processed above  $270^\circ\text{C}$ , while  $\text{Al}(\text{OH})_3$  becomes dehydration at about  $205^\circ\text{C}$ .  $\text{Al}(\text{OH})_3$  will generate bubble in plastics. The surface of polymer becomes roughness, and the product characters are badly influenced. All of these limit its use range.

John M. Stinson and William E. Horn tested fire retardation of a type of modified  $\text{Al}(\text{OH})_3$  ATH which was developed by Alcoa Technical Center (see Journal of Vinyl & Additive Technology, June 1995, Vol.1, No.2, pp.94~97). This kind of modified  $\text{Al}(\text{OH})_3$  has a relative good property, but the article does not disclose any detail of the preparation method about the modified  $\text{Al}(\text{OH})_3$ .

So it is necessary to develop a kind of  $\text{Al}(\text{OH})_3$ , which has good thermo- stability and high initial weight loss temperature, and naturally, the preparation method of such product.

### summary of the invention

The present invention provides an ultrafine modified  $\text{Al}(\text{OH})_3$  whose XRD spectrum has diffraction peaks at the points where D value is 6.39, 6.16, 4.67 Å(Angstrom), and  $2\theta$  angle is 13.836, 14.347, and 19.006 respectively.

The present invention also provides a preparation method of ultrafine modified  $\text{Al}(\text{OH})_3$ , which comprises the steps as follows:

(A) Introducing a  $\text{CO}_2$ -containing gas and a  $\text{NaAlO}_2$  solution into a high gravity rotating bed apparatus (Rotating Packed Beds Reactor(RPBR))to react to form a gel or suspending liquid, after filtering and washing, a  $\text{Al}(\text{OH})_3$  filter cake being obtained which optionally is dried to obtain powder product; wherein the gas/liquid volume flow rate is 0.5~10, on the basis of standard pure  $\text{CO}_2$ ; and the concentration of  $\text{NaAlO}_2$  is 0.1~10 mol/L, preferably is about 1~8 mol/L, and more preferably is 1~5 mol/L; and

(B) Mixing  $\text{Al}(\text{OH})_3$  obtained in Step A, in the form of filter cake or powder, with modifying agents selected from the group consisting of oxalate, oxalic acid or mixture thereof to react for a predetermined period of time at the temperature equal to or higher than  $100^\circ\text{C}$  ( $\geq 100^\circ\text{C}$ ) and drying the outcome to obtain ultrafine modified  $\text{Al}(\text{OH})_3$  powder product.

The present invention also relates to an ultrafine modified  $\text{Al}(\text{OH})_3$  precursor and its preparation method. This method comprises the following steps: introducing a  $\text{CO}_2$ -containing gas and a  $\text{NaAlO}_2$  solution into a high gravity rotating bed apparatus to react and generate a gel or suspending liquid; and filtering and washing the gel or suspending liquid to obtain  $\text{Al}(\text{OH})_3$  filter cake, which optionally is dried to obtain powder product; wherein the gas/liquid volume flow rate is 0.5~10, on the basis of standard pure  $\text{CO}_2$  and wherein the concentration of  $\text{NaAlO}_2$  is 0.1~10 mol/L, preferably about 1~8 mol/L, and more preferably 1~5 mol/L.

The modified  $\text{Al}(\text{OH})_3$  of the present invention has high initial weight loss temperature and high weight loss rate, which is very suitable for fire retardant. The present invention can control the size of  $\text{Al}(\text{OH})_3$  particle within nanometer grade and make it uniformly distributed in the short reaction time of carbon component decomposition. The

initial weight loss temperature can be raised to 330~380°C, and preferably about 350~380°C. At the same time, the rate of weight loss is up to about 50% before 500°C. So it can be applied to thermoplastic plastics whose processing temperature is over 270°C as fire retardant.

### Brief description of the drawings

FIG.1A and 1B are XRD patterns of modified  $\text{Al}(\text{OH})_3$  of the invention.

FIG.2 is TA and TDA curves of modified  $\text{Al}(\text{OH})_3$  of the invention.

FIG.3 is FTIR spectra of modified  $\text{Al}(\text{OH})_3$  of the invention.

FIG.4 is TEM photograph of modified  $\text{Al}(\text{OH})_3$  of the invention.

FIG.5 stands for the process flow chart to prepare modified  $\text{Al}(\text{OH})_3$  of the invention.

FIG.6 is TEM photograph of ultrafine  $\text{Al}(\text{OH})_3$  gel which is the precursor(product in Step A)of modified  $\text{Al}(\text{OH})_3$  of the invention.

FIG.7 stands for the schematic diagram of high gravity rotating beds apparatus in the invention.

### Detailed description of the invention

The present invention provides an ultrafine modified  $\text{Al}(\text{OH})_3$ , whose XRD spectrum has diffraction peaks at the points that D values are 6.39, 6.16, 4.67Å, and  $2\theta$  are 13.836, 14.347, and 19.006 respectively. The intensity of diffraction peaks where  $2\theta$  are 13.836 and 19.006 are 29.12% and 56.10% of the intensity of diffraction peak where  $2\theta$  is 14.347.

FIG.1A and 1B are XRD patterns of modified  $\text{Al}(\text{OH})_3$  of the invention. The modified  $\text{Al}(\text{OH})_3$  of the present invention has intense diffraction peaks at several points where D values are 6.39, 6.16, 6.12, 4.67, 3.70 and 1.99Å, et al. The diffraction peaks where D values are 6.16, 2.36, and 1.86Å are close to  $\gamma\text{-AlOOH}$  (21-1307), while the diffraction peaks where D values are 4.67, 4.24, 3.22, 2.44, 2.07, 1.80, and 1.74Å, are close to  $\text{Al}(\text{OH})_3$  (Gibbsite) (33-18). The diffraction pattern of the product of the present invention does not include other diffraction peaks in the two phases mentioned above. And no known crystalline is found which coincidences to the diffraction peaks at which D values are 6.39, 3.70 and 6.12Å in diffraction pattern of the product of the invention.

According to the invention, the initial weight loss temperature of ultrafine modified  $\text{Al}(\text{OH})_3$  is  $\geq 330^\circ\text{C}$ , preferably is about  $\geq 350^\circ\text{C}$ , and more preferably  $\geq 370^\circ\text{C}$ . For example, the initial weight loss temperature may be 330~380°C, preferably is about 350~380°C, and more preferably is 370~380°C. The rate of weight loss is up to 50% at 500°C, while it is greater than or equal to 51% ( $\geq 51\%$ ) at 600°C. According to the experiments that modified  $\text{Al}(\text{OH})_3$  is applied to PVC, EVA HDPE, PP, PE, ABS, PC, et al. for testing such physical properties as fire retarding and smoke eliminating, the results indicate that ultrafine modified  $\text{Al}(\text{OH})_3$  of the invention can be used to such materials as

PC, PO, PBT et al., to which conventional  $\text{Al}(\text{OH})_3$  can not be applied.

FIG.2 is TA and TDA curves of modified  $\text{Al}(\text{OH})_3$  of the invention. The experimental condition is to heat from 50 to 600 °C at a rate of 10 °C per minute.

FIG.3 is FTIR spectra of modified  $\text{Al}(\text{OH})_3$  of the invention.. The modified  $\text{Al}(\text{OH})_3$  of the invention has adsorption peaks at the points that wave numbers are about 3671.167, 1713.910, 1367.945.

FIG.4 is TEM photograph of modified  $\text{Al}(\text{OH})_3$  of the invention.. Particle size of the ultrafine modified  $\text{Al}(\text{OH})_3$  is very small. The mean particle size is less than 300 nm, preferably less than 250 nm, and more preferably, less than 200 nm. For example, the mean particle size is 300~10 nm, preferably about 250~20 nm and more preferably 150~50 nm .

The density of modified  $\text{Al}(\text{OH})_3$  of the invention is 0.6~1.1 g/cm<sup>3</sup>, preferably about 0.74~1.04 g/cm<sup>3</sup>, while the loose density is 0.5~0.9g/cm<sup>3</sup>, preferably is about 0.54~0.83 g/cm<sup>3</sup>.

The present invention also provides a method of preparing ultrafine modified  $\text{Al}(\text{OH})_3$ , which comprises the steps as follows:

(A) Introducing a CO<sub>2</sub>-containing gas and a NaAlO<sub>2</sub> solution into a high gravity rotating bed apparatus to react to form a gel or suspending liquid, the gel or suspending liquid being filtered and washed to obtain  $\text{Al}(\text{OH})_3$  filter cake, which optionally is dried to obtain powder product; wherein the gas/liquid volume flow rate is 0.5~10, on the basis of standard pure CO<sub>2</sub>; and the concentration of NaAlO<sub>2</sub> is 0.1~10 mol/L, preferably is about 1~8 mol/L, and more preferably is 1~5 mol/L; and

(B) Mixing  $\text{Al}(\text{OH})_3$  obtained in Step A, in the form of filter cake or powder, with modifying agents selected from the group consisting of oxalate, oxalic acid or mixture thereof to react for a predetermined period of time at the temperature equal to or higher than 100°C ( $\geq 100^\circ\text{C}$ ) and drying the outcome to obtain ultrafine modified  $\text{Al}(\text{OH})_3$  powder product.

In particular, the method of preparing ultrafine modified aluminum hydroxide according to the invention basically consists of two steps: carbon component decomposition under condition of high gravity field in high gravity rotating bed apparatus and modification treatment. The concrete steps are described as follows:

**A: Carbon component decomposition:** Introducing a CO<sub>2</sub>-containing gas and a NaAlO<sub>2</sub> solution into a high gravity rotating bed apparatus from gas inlet and liquid inlet respectively. Carbon component decomposition reaction is carried out in the porous packing layers inside the rotating beds. Rotating speed of the rotor of a high gravity rotating bed apparatus is 100~10000 rpm. The gas/liquid volume rate is 0.5~10, on the basis of standard pure CO<sub>2</sub>. The concentration of NaAlO<sub>2</sub> is 0.1~10 mol/L. Gel (suspending liquid) leaves out of the high gravity rotating bed apparatus via liquid outlet after the completion of the reaction.

**B *Modification treatment*:** Filtering and washing the gel (precipitation) in Step A to obtain a filter cake. Mixing the filter cake (or its dried powder after drying) with oxalic acid or/and oxalate (solution and/or solid) to react over 5 min at the reaction temperature of not less than 100 °C. After the modification, the product is treated by such post-treatments as filtering and drying to get modified nano-Al(OH)<sub>3</sub>.

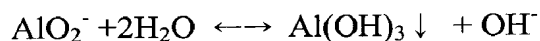
FIG.5 stands for the process flow chart to prepare modified Al(OH)<sub>3</sub> of the invention.

The essence of carbon component decomposition reaction is:

(1) First, because of the strong basicity of NaAlO<sub>2</sub> solution, the introduced CO<sub>2</sub> can neutralize hydroxyl (OH<sup>-</sup>) in the solution. That is:



(2) Then, for the sake of neutralization of CO<sub>2</sub>, NaAlO<sub>2</sub> solution loses its stability, and decompose and precipitate out Al(OH)<sub>3</sub>. That is:



The main purpose of carbon component decomposition process is to prepare a uniform gel (precipitation) for the next modification step.

Carbon component decomposition process of step A of the present invention has not special requirement of reaction temperature, but it is preferable that the reaction of step A is carried out at the temperature of 15~100 °C, more preferably about 20~80 °C, and more preferably from 30~70 °C.

Rotating speed of the rotor of rotating beds can vary in a wide range, for instance 100~10000 rpm, preferably about 150~5000 rpm, and more preferably 200~3000 rpm.

In Step A, the CO<sub>2</sub>-containing gas mentioned above can be CO<sub>2</sub> of industrial purity or a mixture containing CO<sub>2</sub>. The starting CO<sub>2</sub> content is preferable  $\geq 10\%$ . The gas/liquid volume rate is 0.1~5, on the basis of standard pure CO<sub>2</sub>.

In Step A, pH value of gel or suspending liquid should be controlled  $\geq 8$ , preferably  $\geq 11.5$ , for example pH=8~13 or 8.5~12.5.

The porous packing layers in Step A of the invention has not special requirement too. Porous plate, mesh, foam material and regular packing are all suitable to the present invention.

Reaction time in Step A can vary in a wide range, depending on the quantity of reactant and the volume of reactor, and etc. The reaction time is usually 5~60 min, preferably about 5~30 min.

Moreover, activator and crystal form controlling agent can also be added in Step A, which cause full dispersion of particle, refine and narrow the distribution of particle size, and control the shape of modified Al(OH)<sub>3</sub> precursor. The mentioned activator can be for example fatty acid, and crystal form control agent is sulfate or phosphate. It is no doubt to use any other common activator and crystal form controlling agent which were known in

this art.

FIG.7 stands for the schematic diagram of high gravity rotating bed apparatus according to the invention. The apparatus was described in detail in Chinese Patent No. ZL95105343.4, which is incorporated herein as a reference.

The modifying agent used in Step B of the invention is oxalate, oxalic acid or their mixture, which can be used in the form of solution or crystal. The examples of the oxalate include lithium, sodium and potassium oxalate.

The  $\text{Al}(\text{OH})_3$  used in Step B is  $\text{Al}(\text{OH})_3$  gel or powder which is formed in the process of carbon component decomposition in Step A. The molar ratio of modifying agent in Step B to  $\text{Al}(\text{OH})_3$  filter cake or powder from Step A is 0.3~2, preferably about 0.5~1.5, and more preferably from 0.8 to 1.2. And the mentioned modifying agent can be used in the form of solid or solution.

The temperature of modifying process in Step B is more than 100 °C, for example 100~205 °C, and preferably from 140~180 °C.

Reaction time in Step B can alternate in a wide range, depending on the quantity of reactant and the volume of reactor. The reaction time in Step B is usually 5 min~5 hr, preferably about 10 min~2 hr, and more preferably 30 min~1.5 hr.

In the modification process of Step B of the invention, activator and crystal form controlling agent can also be added to cause full dispersion of particle, to refine and narrow the distribution of particle size, and to control the shape of modified  $\text{Al}(\text{OH})_3$  precursor. The examples of the activator include fatty acid or salt, ester aluminate, ester titanate, and etc. The crystal form controlling agent is sulfate or phosphate. It is no doubt to use any other common activator and crystal form controlling agent which were known in the art.

The present invention also provides a method of preparing ultrafine  $\text{Al}(\text{OH})_3$ , which comprising the following steps: introducing a  $\text{CO}_2$ -containing gas and a  $\text{NaAlO}_2$  solution into a high gravity rotating bed apparatus to react and generate a gel or suspending liquid; filtering and washing the gel or suspending liquid to obtain  $\text{Al}(\text{OH})_3$  filter cake, which optionally is dried to obtain powder product; wherein the gas/liquid volume flow rate is 0.5~10, on the basis of standard pure  $\text{CO}_2$  and wherein the concentration of sodium aluminate ( $\text{NaAlO}_2$ ) is 0.1~10 mol/L, preferably about 1~8 mol/L, and more preferably 1~5 mol/L.

The ultrafine  $\text{Al}(\text{OH})_3$  according to the method can be used as precursor of modified  $\text{Al}(\text{OH})_3$  of the present invention. FIG.6 is TEM photograph of ultrafine  $\text{Al}(\text{OH})_3$  gel which is the precursor (product in Step A) of the modified  $\text{Al}(\text{OH})_3$  of the invention.

The present invention also provides a fire retardant product, which comprises the modified ultrafine  $\text{Al}(\text{OH})_3$  of the present invention. According to the experiments that modified  $\text{Al}(\text{OH})_3$  is applied to PVC, EVA HDPE, PP, PE, ABS, PC, et al. for testing the physical properties such as fire retarding and smoke eliminating, the results indicate that

ultrafine modified  $\text{Al}(\text{OH})_3$  of the invention can be used in such materials as PC, PO, PBT et al., to which conventional  $\text{Al}(\text{OH})_3$  can not be applied.

The followings are examples to illustrate the present invention, but, these examples, by no means, limit the scope of the invention.

#### *Example 1*

Preparing an aqueous solution of  $\text{NaAlO}_2$  with a concentration of 2.18 mol/L. The solution was filtered to remove the impurities and placed in **circulating tank** 13. The solution was pumped by **pump** 12 to **liquid inlet** 6 of rotating beds and entered into **porous packing layer** 8 at the temperature of  $35^\circ\text{C}$  via **distributor** 9.  $\text{CO}_2$  gas after being decompressed from gas cylinder was introduced to the rotating bed continuously from **gas inlet** 4. The gas/liquid volume flow rate was adjusted to 1.25. At this moment, a carbon component decomposition reaction take place between  $\text{CO}_2$  and  $\text{NaAlO}_2$  solution in the **packing layer** 8 of the beds to form a gel. The rotating speed of the rotor of the rotating bed was controlled about 2100 rpm. Liquid which has not completely reacted flows to **circulating tank** 13 thru **liquid outlet** 7, and recycled by circulating pump to react with  $\text{CO}_2$  in the rotating bed constantly. When pH of gel liquid becomes 12, carbon component decomposition reaction accomplishes. The TEM photograph of gel was shown in FIG.6. After filtering and washing, the gel was mixed with oxalic acid solution at a molar ratio of the gel: oxalic acid solution=1:0.87 to form a solution with  $\text{Al}(\text{OH})_3$  being about 46.3g/L so as to carry out modifying reaction. Reaction temperature was  $150^\circ\text{C}$ , while reaction time was 4~5 hr. The liquid product was filtered, washed and dried after reaction finishes, and modified  $\text{Al}(\text{OH})_3$  was obtained. The TEM photograph of the modified  $\text{Al}(\text{OH})_3$  was shown in FIG.4, and TG/TGA of the modified  $\text{Al}(\text{OH})_3$  were shown in FIG.3.

Chemical element analysis of the modified product: Al 24.86%, O 34.55%, C 11.86%, H 2.28%.

#### *Example 2*

The reaction was carried out in the same manner as *example 1*, except that 14.5g  $\text{Al}(\text{OH})_3$  from carbon component decomposition reaction and 0.5mol oxalic acid (350ml) form a solution (550ml) by adding water.

The density of modified  $\text{Al}(\text{OH})_3$  product was  $0.8 \text{ g/cm}^3$ , and specific surface area was  $13 \text{ m}^2/\text{g}$ .

#### *Example 3*

The reaction was carried out in the same manner as *example 2*, except that a  $\text{NaAlO}_2$  solution with the concentration being 3.5 mol/L was used to prepare  $\text{Al}(\text{OH})_3$

precursor, and 21.1g  $\text{Al}(\text{OH})_3$  precursor obtained from carbon component decomposition reaction was mixed with 510 ml oxalic acid to form a solution (800 ml) by adding water. The time for modification is 90~120 min.

*Example 4*

The reaction was carried out in the same manner as *example 2*, except that 14.5g  $\text{Al}(\text{OH})_3$  from carbon component decomposition reaction was mixed with 81 gram oxalic acid (350ml) to form a solution (800 ml) by adding water and that the time for modification was 45~60min.

*Example 5*

The reaction was carried out in the same manner as *example 2*, except that 129 g filter cake of  $\text{Al}(\text{OH})_3$  from carbon component decomposition reaction was mixed with 1162 gram oxalic acid (350ml) to form a solution (800 ml) by adding water and the time for modification was 20-30 min.

*Example 6*

The reaction was carried out in the same manner as *example 2*, except that a  $\text{NaAlO}_2$  solution (3.5 mol/L) was used to prepare  $\text{Al}(\text{OH})_3$  precursor, and 200 g  $\text{Al}(\text{OH})_3$  filter cake obtained from carbon component decomposition reaction was mixed with 226.5 g oxalic acid to form a solution (800 ml) by adding water and the time for modification was 15~20 min.

*Example 7*

The reaction was carried out in the same manner as *example 6*, except that the reaction of modification was carried out for 210~270 min under 120°C.

*Example 8*

The reaction was carried out in the same manner as *example 6*, except that the reaction of modification was carried out for 60-90 min under 135 °C.

*Example 9*

The reaction was carried out in the same manner as *example 6*, except that the reaction of modification was carried out for 5-10 min under 165 °C.

TEM photographs and TA/DTA curves of the modified  $\text{Al}(\text{OH})_3$  and precursors obtained in *example 2~9* are similar to FIG.1~5.



The present invention was described by the examples, but the present invention is not limited to these examples. One of ordinary in the art may make modifications based on the present invention, which are within the scope of the claims attached therein.

## Claims

1. An ultrafine modified  $\text{Al}(\text{OH})_3$  having diffraction peaks of X-ray diffraction (XRD) spectrum at the locations that D values are 6.39, 6.16, 4.67 Å, and  $2\theta$  are 13.836, 14.347, and 19.006 respectively.

2. An ultrafine modified  $\text{Al}(\text{OH})_3$  of Claim 1, wherein the intensities of diffraction peaks where  $2\theta$  are 13.836 and 19.006 are 29.12% and 56.10% of the diffraction peak where  $2\theta$  is 14.347.

3. An ultrafine modified  $\text{Al}(\text{OH})_3$  of Claim 1, wherein the initial weight loss temperature is 330~380°C, preferably is about 350~370°C; and the rate of weight loss is up to 51% at 600°C.

4. An ultrafine modified  $\text{Al}(\text{OH})_3$  of Claim 1, wherein the mean particle size is less than 300nm, preferably, less than 250nm, and more preferably less than 200nm.

5. An ultrafine modified  $\text{Al}(\text{OH})_3$  of Claim 1, wherein the mean particle size is 300~10 nm, preferably about 250~20 nm, and more preferably 150~50 nm.

6. An ultrafine modified  $\text{Al}(\text{OH})_3$  of Claim 1, wherein said density is 0.6~1.1 g/cm<sup>3</sup>, preferably about 0.74~1.04g/cm<sup>3</sup> and the loose density is 0.5~0.9 g/cm<sup>3</sup>, preferably about 0.54~0.83 g/cm<sup>3</sup>.

7. A method of preparing ultrafine modified  $\text{Al}(\text{OH})_3$ , which comprises the steps as follows:

(A) Introducing a CO<sub>2</sub>-containing gas and a NaAlO<sub>2</sub> solution into a high gravity rotating bed apparatus to react and form a gel or suspending liquid, said gel or suspending liquid be filtered and washed to obtain a  $\text{Al}(\text{OH})_3$  filter cake, which optionally is dried to obtain a powder product; wherein the gas/liquid volume flow rate is 0.5~10, on the basis of standard pure CO<sub>2</sub>; and the concentration of NaAlO<sub>2</sub> is 0.1~10 mol/L, preferably is about 1~8 mol/L, and more preferably is 1~5 mol/L; and

(B) Mixing  $\text{Al}(\text{OH})_3$  in the form of filter cake or powder obtained in Step A with modifying agents selected from the group consisting of oxalate, oxalic acid or mixture thereof to react for a predetermined time at the temperature equal to or higher than 100°C and drying the outcome to obtain the desired ultrafine modified  $\text{Al}(\text{OH})_3$  powder product.

8. A method of Claim 7, wherein the reaction temperature in Step B is less than 205°C, preferably is 140-180°C.

9. A method of Claim 7, wherein the molar ratio of modifying agents in Step B to  $\text{Al}(\text{OH})_3$  filter cake or powder from Step A is 0.3~2, preferably about 0.5~1.5, more preferably 0.8-1.2; and said modifying agents are in the form of solid or solution.

10. A method of Claim 7, wherein the gas/liquid volume rate is 0.1~5 in Step A, on the basis of standard pure CO<sub>2</sub>, and the reaction temperature is 20~80°C.

11. A method of Claim 7, wherein pH value of gel or suspending liquid should be

controlled to  $\geq 8$  in Step A, preferably  $\geq 11.5$ , for example pH=8~13 or 8.5~12.5.

12. A method of Claim 7, wherein said oxalate is lithium, sodium and potassium oxalate.

13. A method of Claim 7, wherein said activator and/or crystal form controlling agent(s) are added into Step A and/or Step B and said activator is selected from the group consisting of fatty acid or salt, ester aluminate or ester titanate, and said crystal form controlling agent is selected from sulfate or phosphate.

14. A method of preparing ultrafine  $\text{Al}(\text{OH})_3$ , comprising the following steps: introducing a  $\text{CO}_2$ -containing gas and a  $\text{NaAlO}_2$  solution into a high gravity rotating bed apparatus to react and generate a gel or suspending liquid; and filtering and washing said gel or suspending liquid to obtain  $\text{Al}(\text{OH})_3$  filter cake, which optionally is dried to obtain powder product; wherein the gas/liquid volume flow rate is 0.5~10, on the basis of standard pure  $\text{CO}_2$  and wherein the concentration of  $\text{NaAlO}_2$  is 0.1~10 mol/L, preferably about 1~8 mol/L, and more preferably 1~5 mol/L.

15. A method of Claim 14, wherein, pH value of gel or suspending liquid is  $\geq 8$ , preferably,  $\geq 11.5$ , for example pH=8~13 or 8.5~12.5.

16. An ultrafine  $\text{Al}(\text{OH})_3$  product prepared by the method of either of Claim 14~15.

17. A fire retardant product comprising ultrafine modified  $\text{Al}(\text{OH})_3$  according to any one of Claimd 1~6 as fire retardant.

18. Use of ultrafine modified  $\text{Al}(\text{OH})_3$  obtained by the method of any one of Claims 1~6 in fire retardant product as fire retardant.

## **Abstract**

This invention relates to a method of preparing ultrafine modified aluminium hydroxide, which includes two steps: carbon component decomposition under ultragravity condition in rotating bed and modifying treatment. The carbon component decomposition of the present invention is carried out in the porous packing layer inside of the rotating bed and a mass transfer for the reaction and micro-mixing process are extremely enhanced, and the aluminium hydroxide sol (precipitate or/and dry powder) obtained is further converted by the subsequent modified treatment process. This method can control particle size of the modified aluminium hydroxide crystal grains, homogenize its distribution and shorten the reaction time. Particularly, the modified treatment greatly improves its weight loss temperature and weight loss ratio. It extremely expands the use field of aluminium hydroxide as flame retardant and etc. Average size of modified aluminium hydroxide grain obtained is from 50 nm to several micrometers and can be controlled. Its grain size can be homogeneously distributed and nano-graded. It improves the mechanical properties of polymers. The process of the present invention is conveniently used in industries and can improve productivity and the product grade.

FIG.1A XRD patterns of modified  $\text{Al}(\text{OH})_3$  of the invention(enlarged)

FIG.1B XRD patterns of modified  $\text{Al}(\text{OH})_3$  of the invention.

FIG.2 TA and TDA curves of modified  $\text{Al}(\text{OH})_3$  of the invention.

sample, thermoanalysis, start, peak, weight (%), derivative weight (%/minute),  
temperature,  
heat from 50 to 600°C as a rate of 10°C per minute.

FIG.3 FTIR spectra of modified  $\text{Al}(\text{OH})_3$  of the invention.

Transparency, wave number

FIG.4 TEM photograph of modified  $\text{Al}(\text{OH})_3$  of the invention.

FIG.5 Process flow chart to prepare modified  $\text{Al}(\text{OH})_3$  of the invention.

sodium aluminate ( $\text{NaAlO}_2$ ) solution + carbon dioxide  $\text{CO}_2$  — RPBR — gel —  
filter + wash — aluminum hydroxide ( $\text{Al}(\text{OH})_3$ ) + Hydrothermal modification —  
modified ATH — wash/dry — product

FIG.6 TEM photograph of ultrafine  $\text{Al}(\text{OH})_3$  gel which is the precursor compound (product  
in Step A)of modified  $\text{Al}(\text{OH})_3$  of the invention.

FIG.7 Schematic diagram of high gravity rotating bed apparatus in the invention.

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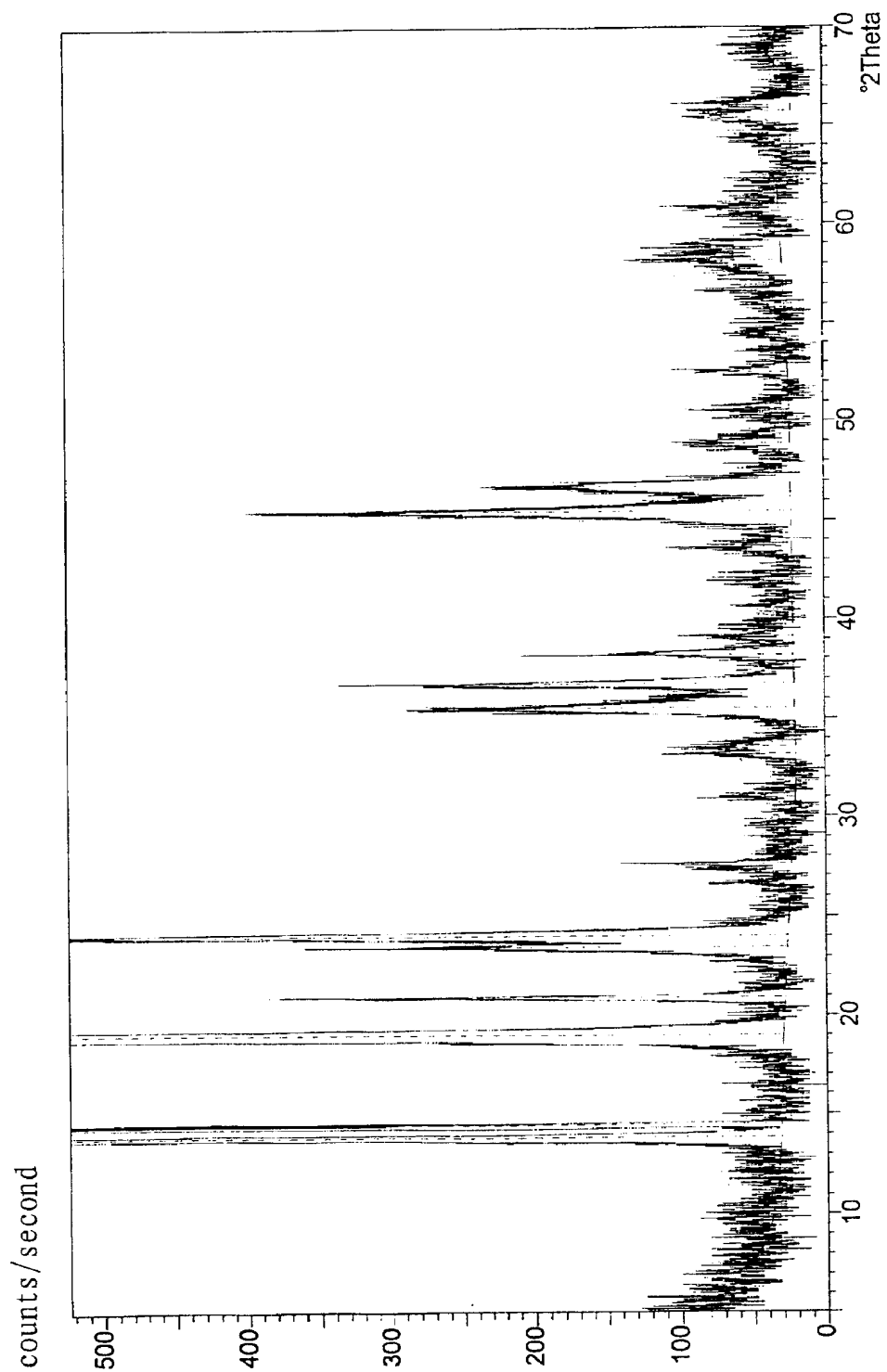


FIG. 1A XRD patterns of modified Al(OH)<sub>3</sub> of the invention(enlarged)

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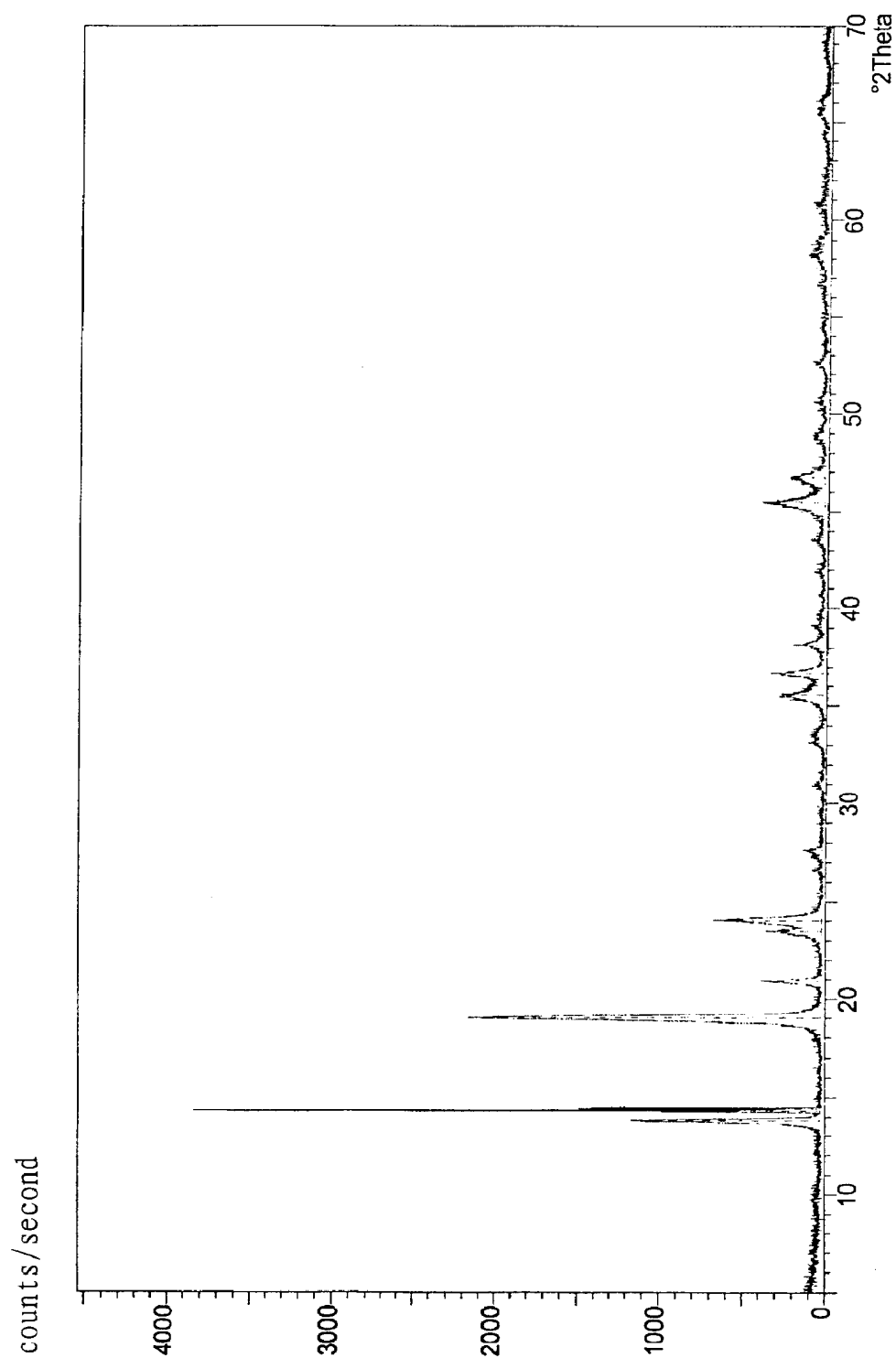


FIG. 1B XRD patterns of modified Al(OH)<sub>3</sub> of the invention.

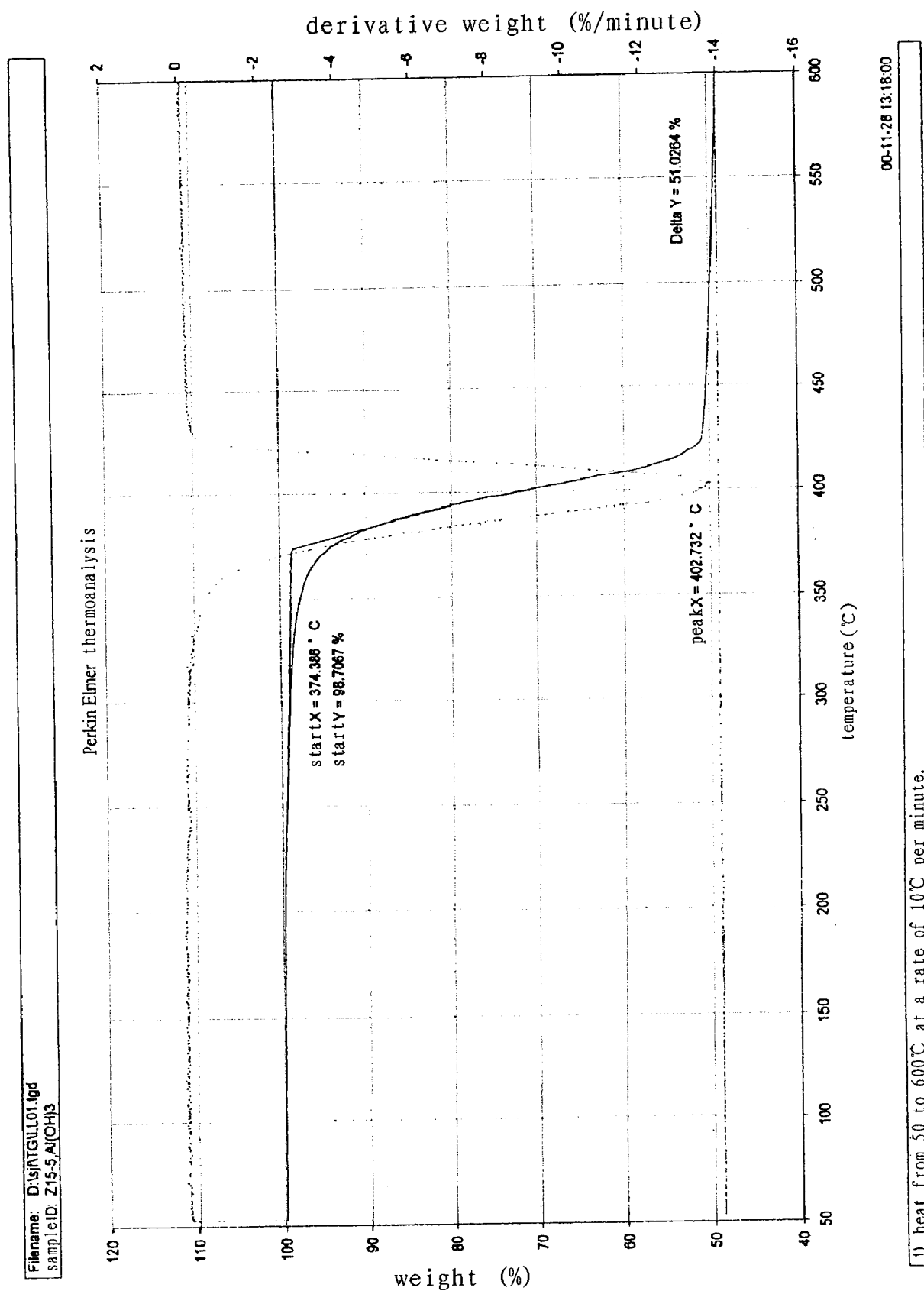


FIG. 2 TA and TDA curves of modified Al(OH)3 of the invention.



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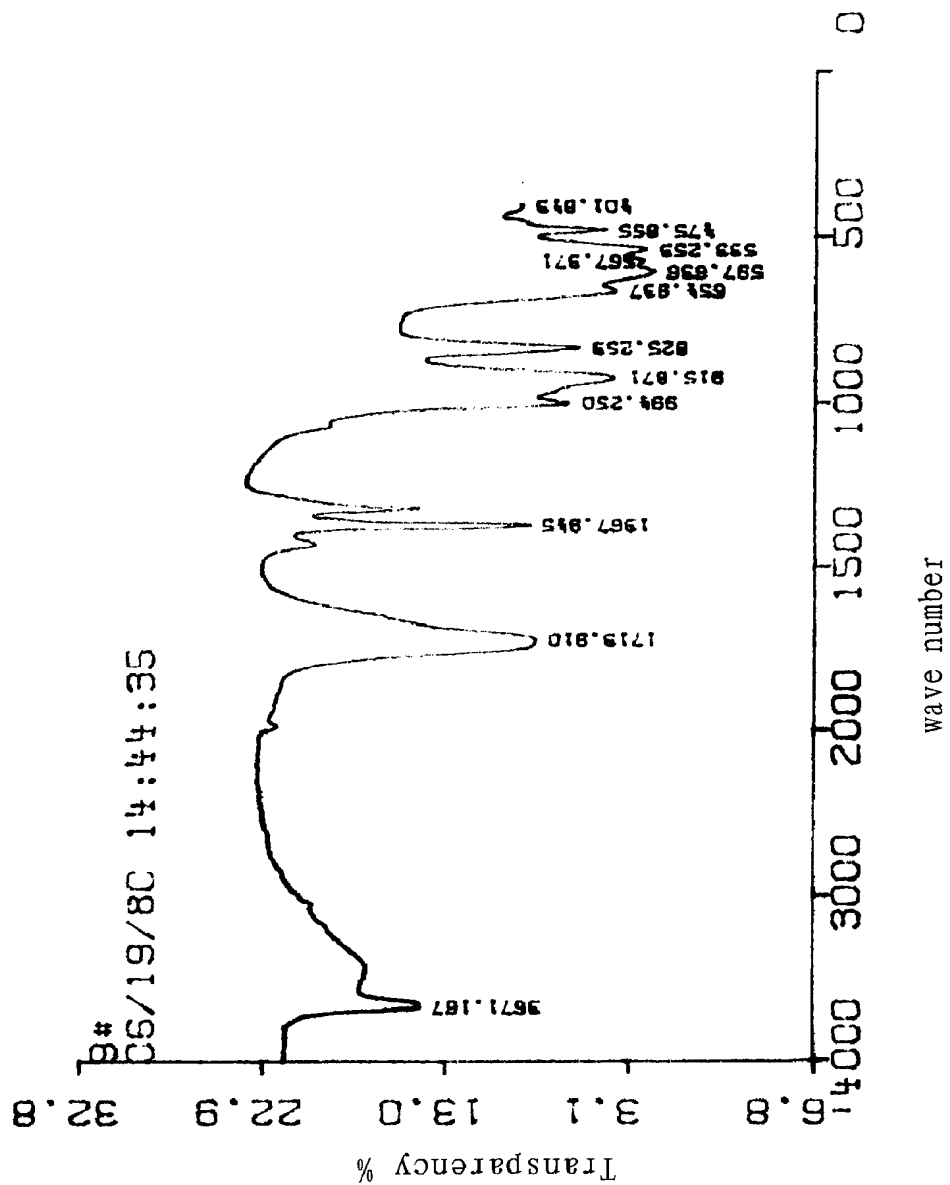


FIG. 3 FTIR spectra of modified Al(OH)<sub>3</sub> of the invention.

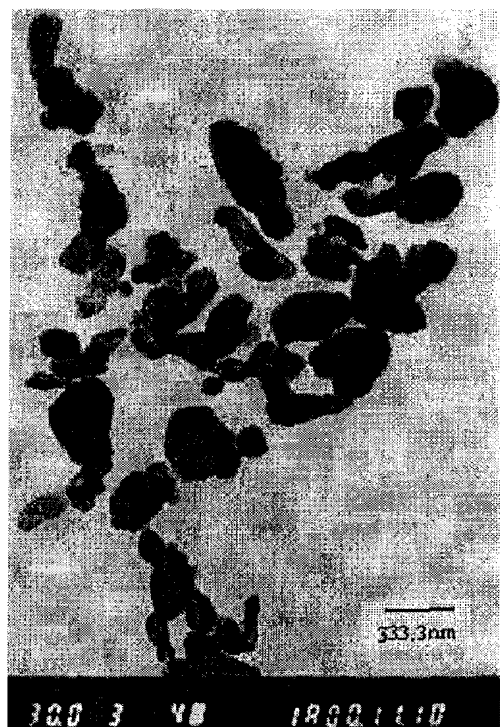


FIG. 4 TEM photograph of modified  $\text{Al}(\text{OH})_3$  of the invention.



FIG. 6 TEM photograph of ultrafine  $\text{Al}(\text{OH})_3$  gel which is the precursor compound (product in Step A) of modified  $\text{Al}(\text{OH})_3$  of the invention.

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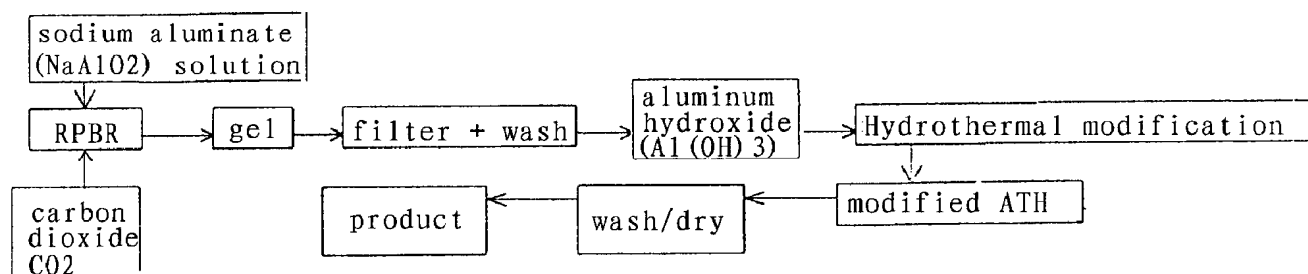


FIG. 5 Process flow chart to prepare modified Al(OH)<sub>3</sub> of the invention.

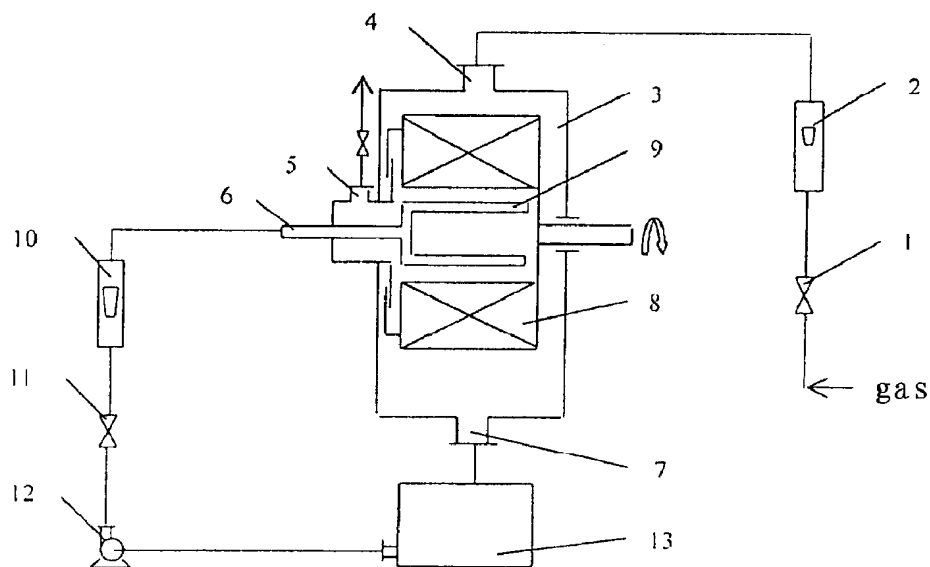


FIG. 7 Schematic diagram of high gravity rotating bed apparatus in the invention.

From the INTERNATIONAL BUREAU

**PCT**NOTICE INFORMING THE APPLICANT OF THE  
COMMUNICATION OF THE INTERNATIONAL  
APPLICATION TO THE DESIGNATED OFFICES

(PCT Rule 47.1(c), first sentence)

To:

LIU, SHEN & ASSOCIATES  
A0601, Huibin Building No. 8  
Beichen Dong Street, Chaoyang District  
Beijing 100101  
CHINE

RECEIVED

10 DEC 2002

LIU, SHEN

Date of mailing(day/month/year) 28 November 2002 (28.11.02)		IMPORTANT NOTICE	
Applicant's or agent's file reference IPY2700			
International application No. PCT/CN01/000810	International filing date(day/month/year) 18 May 2001 (18.05.01)	Priority date(day/month/year)	
Applicant BEIJING UNIVERSITY OF CHEMICAL TECHNOLOGY, et al			

1. Notice is hereby given that the International Bureau has **communicated**, as provided in Article 20, the international application to the following designated Offices on the date indicated above as the date of mailing of this notice:

KP, KR, US

In accordance with Rule 47.1(c), third sentence, those Offices will accept the present notice as conclusive evidence that the communication of the international application has duly taken place on the date of mailing indicated above and no copy of the international application is required to be furnished by the applicant to the designated Office(s).

2. The following designated Offices have waived the requirement for such a communication at this time:

AE, AG, AL, AM, AP, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EA, EE, EP, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, OA, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, UZ, VN, YU, ZA, ZW

The communication will be made to those Offices only upon their request. Furthermore, those Offices do not require the applicant to furnish a copy of the international application (Rule 49.1(a-bis)).

3. Enclosed with this notice is a copy of the international application as published by the International Bureau on 28 November 2002 (28.11.02) under No. WO 02/094715.

**4. TIME LIMITS for filing a demand for international preliminary examination and for entry into the national phase**

The applicable time limit for entering the national phase will, **subject to what is said in the following paragraph**, be **30 MONTHS** from the priority date, not only in respect of any elected Office if a demand for international preliminary examination is filed before the expiration of **19 months** from the priority date, but also in respect of any designated Office, in the absence of filing of such demand, where Article 22(1) as modified with effect from 1 April 2002 applies in respect of that designated Office. For further details, see *PCT Gazette* No. 44/2001 of 1 November 2001, pages 19926, 19932 and 19934, as well as the *PCT Newsletter*, October and November 2001 and February 2002 issues.

In practice, **time limits other than the 30-month time limit** will continue to apply, for various periods of time, in respect of certain designated or elected Offices. For **regular updates on the applicable time limits** (20, 21, 30 or 31 months, or other time limit), Office by Office, refer to the *PCT Gazette*, the *PCT Newsletter* and the *PCT Applicant's Guide*, Volume II, National Chapters, all available from WIPO's Internet site, at <http://www.wipo.int/pct/en/index.html>.

For filing a **demand for international preliminary examination**, see the *PCT Applicant's Guide*, Volume I/A, Chapter IX. Only an applicant who is a national or resident of a PCT Contracting State which is bound by Chapter II has the right to file a demand for international preliminary examination (at present, all PCT Contracting States are bound by Chapter II).

It is the applicant's **sole responsibility** to monitor all these time limits.

The International Bureau of WIPO 34, chemin des Colombettes 1211 Geneva 20, Switzerland	Authorized officer  Judith Zahra
Facsimile No.(41-22) 740.14.35	Telephone No.(41-22) 338.91.11

## PATENT COOPERATION TREATY

PCT

INFORMATION CONCERNING ELECTED  
OFFICES NOTIFIED OF THEIR ELECTION

(PCT Rule 61.3)

From the INTERNATIONAL BUREAU

To:

LIU, SHEN & ASSOCIATES  
A0601, Huibin Building No. 8  
Beichen Dong Street, Chaoyang  
Distric  
Beijing 100101  
China

Date of mailing (day/month/year)

15 January 2003 (15.01.03)

Applicant's or agent's file reference

IIPY2700

## IMPORTANT INFORMATION

International application No.

PCT/CN01/00810

International filing date (day/month/year)

18 May 2001 (18.05.01)

Priority date (day/month/year)

Applicant

BEIJING UNIVERSITY OF CHEMICAL TECHNOLOGY et al

1. The applicant is hereby informed that the International Bureau has, according to Article 31(7), notified each of the following Offices of its election:

EP : AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR

National : AU, BG, CA, CN, DE, GB, IL, JP, KP, KR, MN, NO, PL, RO, RU, SK, US

2. The following Offices have waived the requirement for the notification of their election; the notification will be sent to them by the International Bureau only upon their request:

AP : GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW

EA : AM, AZ, BY, KG, KZ, MD, RU, TJ, TM

OA : BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG

National : AE, AG, AL, AM, AT, AZ, BA, BB, BR, BY, BZ, CH, CO, CR, CU, CZ, DK, DM, DZ, EE, ES, FI, GD, GE, GH, GM, HR, HU, ID, IN, IS, KE, KG, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MW, MX, MZ, NZ, PT, SD, SE, SG, SI, SL, TJ, TM, TR, TT, TZ, UA, UG, UZ, VN, YU, ZA, ZW

3. The applicant is reminded that he must enter the "national phase" **before the expiration of 30 months from the priority date** before each of the Offices listed above. This must be done by paying the national fee(s) and furnishing, if prescribed, a translation of the international application (Article 39(1)(a)), as well as, where applicable, by furnishing a translation of any annexes of the international preliminary examination report (Article 36(3)(b) and Rule 74.1).

Some offices have fixed time limits expiring later than the above-mentioned time limit. For detailed information about the applicable time limits and the acts to be performed upon entry into the national phase before a particular Office, see Volume II of the PCT Applicant's Guide.

The entry into the European regional phase is postponed **until 31 months from the priority date** for all States designated for the purposes of obtaining a European patent.

The International Bureau of WIPO  
34, chemin des Colombettes  
1211 Geneva 20, Switzerland

Facsimile No. (41-22) 338.89.65

Authorized officer:

Marek LASKOWSKI (Fax 338.89.65)

Telephone No. (41-22) 338 8152